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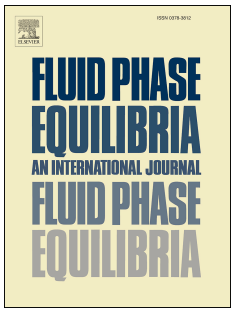

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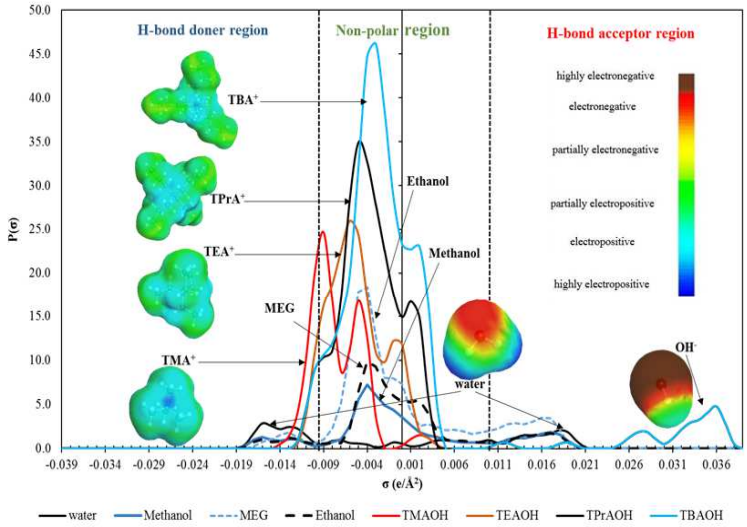
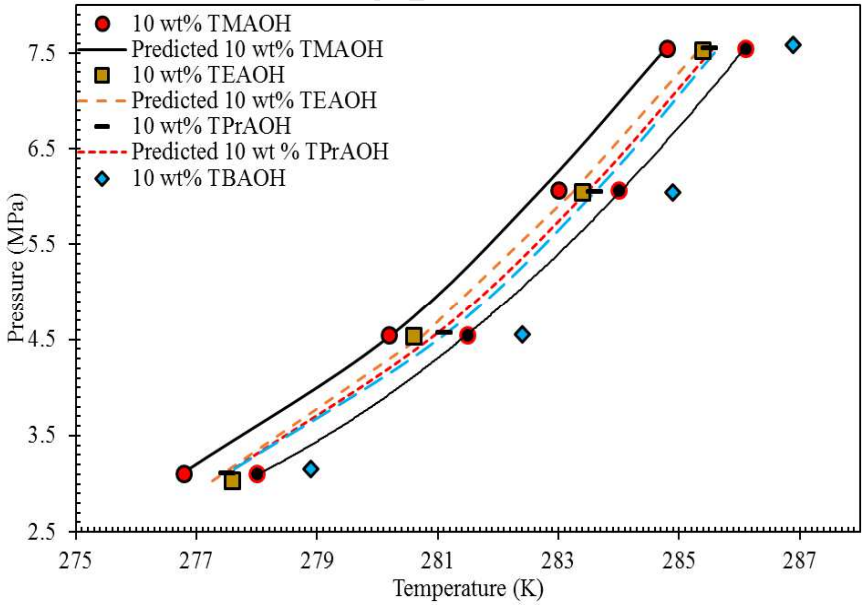
Graphical Abstract





Experimental Evaluation and Thermodynamic Modelling of AILs Alkyl Chain Elongation on Methane Riched Gas hydrate System

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Abstract

In this study, the thermodynamic inhibition of CH_4 rich binary mixed hydrate system (70-30 mole% CH_4 + CO_2) is reported for four ammonium based ionic liquids (AILs) via experimental and modelling approaches. The T-cycle technique applied for the characterization of the AILs namely tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), tetrapropyl ammonium hydroxide (TPrAOH) and tetrabutylammonium hydroxide (TBAOH). The hydrate liquid-vapour equilibrium (HL_wVE) conditions of studied systems measure within the temperature and pressure ranges of 275.0-286.0 K and 3.0 – 7.50 MPa respectively at 10wt% aqueous AILs solutions. All the studied AILs except TBAOH inflicted the THI influence by shifting the HL_wVE of CH_4 enrich mixed gas hydrates. Elongation in AILs alkyl chain length attributed to decrease the average hydrate suppression temperature (ΔT). At 10 wt%, TMAOH exhibited the maximum inhibition impact with a ΔT value of 1.28 K, followed by TEAOH (0.8 K), TPrAOH (0.7 K), and TBAOH (-0.84 K) respectively. Instead of hydrate inhibitor, TBAOH worked as gas hydrate promotor owing to the presence of relatively higher alkyl chain cation (butyl) make it semi-clathrate hydrate. The study further extended for different concentrations (1, 5 and 10 wt%) of TMAOH among the best considered AIL in this study. COSMO-RS investigation is also incorporated to further understand the thermodynamic inhibition behaviour of AILs via sigma profile analysis. Additionally, the enthalpies of hydrate dissociation for all studied AILs systems also calculated via Clausius-Clapeyron equation in this study. The calculated hydrate dissociation enthalpies data revealed that all the studied AILs except TBAOH show insignificant participation in mixed gas hydrate cage formation, therefore, do not form semi-clathrate hydrates. However, enthalpy data of TBAOH revealed that it participated in hydrate crystalline structure, therefore, worked as semi-clathrate hydrate. Furthermore, the HL_wVE predictions of studied systems also performed via electrolyte based model proposed by Dickens and Quinby-Hunt and found in respectable agreement with the experimental data.

Keywords— Ammonium based Ionic Liquids (AILs); alkyl chain; CH_4 rich gas hydrates; HL_wVE, ionic liquids; THI.

INTRODUCTION

Clathrate hydrate or gas hydrate are non-stoichiometric solid crystalline inclusion compound formed due to the hydrogen-bonded water molecules as a host and small size (<10 Å) gas as a guest molecule in thermodynamically favourable environments. Commonly three hydrate structures; sI, sII and sH hydrate are found in nature. Small guest gases like methane (CH_4) and carbon dioxide (CO_2) formed s1 hydrates [1].

Formation of gas hydrates or clathrate hydrates is among the significant flow assurance problems. Gas hydrates formation not solitary averts hydrocarbon production it also obstructs in transportation and processing phases as well [2,3]. As the gas and oil production moves to a more in-depth geographical location where encountered added thermodynamically favourable conditions for hydrate formation, the gas exploration is getting more prone to hydrate happenstances. Additionally, the presence of small impurities, like CO_2, hydrogen sulphide (H_2S) in the CH_4 system leads to further hydrate happenstances. Since CO_2 more prone to hydrate formation; the formation pressure of CO_2 is much lower than the uncontaminated CH_4 systems, therefore, it significantly influenced on phase boundary of CH_4 gas [4].

Oil and gas industry paid enormous expenses; approximately USD 1 million annually per mile for the insulation of off-shore pipelines and further hundreds of million dollars spent on various conventional approaches [5–7]. To avoid gas hydrate formations industry typically practices four common methods heating/insulation of the pipeline, depressurization, removal of water together with chemical insertion. In most of the cases, chemical inhibition is the only viable preventive method applied for gas hydrate mitigation[8]. The chemical inhibitors further divided into thermodynamic inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs).

The THIs (methanol and mono-ethylene glycol (MEG)) applied in massive compositions10-50 wt% to form effective hydrogen bonding with water molecules thus shifts the hydrate phase equilibrium curve towards lower temperature and higher pressure regions to enhance hydrate free zone [9]. The problems related to conventional THIs are their volatile nature together with the large quantities requirements leads the more extensive storage facilities in the off-shore applications. The LDHIs used in lesser quantities 0.50-2.0 wt% than THIs, and are divided into kinetic hydrate inhibitors (KHIs) and Anti Agglomerates (AAs). KHIs typically based

on hydrophilic polymers (Polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) which delays the nucleation and hydrate formation by intermingling at the water-gas interface thus offers steric hindrance between the gas and water. On the other hand, AAs belong to surfactants family; they do not prevent hydrate formation, but they keep tiny hydrate particles into a form of hydrate slurry and are not allow hydrates to agglomerate into large masses (hydrate plugs). The LDHIs found less effective in higher sub-cooling conditions which usually encounter in deeper-water pipelines often attributed to the catastrophic hydrate growth [10].

Therefore, the quest for non-volatile, relatively environmentally friendly, innovative and dual functional hydrate inhibitors leads researchers towards liquid salts, i.e. ionic liquids (ILs). Xiao and Adidharma [11] initially used six imidazolium-based ILs (IMILs) for dual functional gas hydrate inhibitors for CH_4 hydrate. They found that studied ILs can shift hydrate equilibrium conditions towards lower temperature together with delayed hydrate formation. Most of the studied ILs for hydrate inhibition in the literature based on IMIL studies [12–19]. Limited researchers have found on the influence of other ILs families [14,17,20–23] (mainly ammonium based ionic liquids (AILs) [24–29]) for gas hydrate mitigation. Similarly, Keshavarz *et al*. [21] inductee the research on AILs by application of tetraethylammonium chloride (TEACl) with IMILs and found that TEACl provided better THI impact compare to IMILs on CH_4 hydrates.

Tariq *et al*. [30] employed five different families of AILs at lower quantities (1 and 5 wt %) as dual-functional gas hydrate inhibitors for CH_4 hydrates and found that all AILs were able to induce THI influence at moderate temperature condition (3.0-7.0 MPa). However, at higher pressure, the inhibition influence appears to be reduced drastically, and few of the studied AILs disclosed promotional effect as well [30]. In our earlier work, TMAOH was reported as an suitable thermodynamic inhibitor for both pure CH_4 and CO_2 hydrate systems. The inhibition impact, i.e., average suppression temperature (ΔT) of TMAOH was reported as 1.53 and 2.27 K for CH_4 and CO_2 hydrates respectively. Recently our lab also reported TMACl, TEAOH and TPrAOH inhibitions up to 1.7 K, 1.6 K and 1.2 K respectively for CO_2 hydrates [4]. Table 1 represents the ΔT values of various systems for quantitative comparisons purpose.

Table 1: Average suppression temperature (ΔŦ) of 10 wt% considered AILs samples for different systems and comparisons with literature data.

Studied System	***Ŧ* (K)**			
	CH_4 hydrate	**CO_2 hydrate**	**70-30 hydrate**	**CH_4+CO_2**
TMAOH	1.53 [29]	2.27 [29]	1.28 (this study)	
TEAOH	-	1.67 [4]	0.78 (this study)	
TPrAOH	-	1.22 [4]	0.70 (this study)	
TBAOH	-	-	-0.84 (this study)	
Glycine [31,32]	1.78	1.83	-	
Alanine [31,32]	1.55	1.68	-	
Proline [31,32]	1.43	1.44	-	
Serine [31,32]	1.29	1.21	-	
Arginine [31,32]	0.74	1.03	-	
[OH-EMIM][Cl] [33]	1.70	-	-	
Triethylene Glycol [34]	1.28	-	-	
Mono Ethylene Glycol [35]	2.59		-	
Mono Ethylene Glycol (CSMGem)	2.49	2.61	2.51	
Methanol [35]	4.70	-	-	
Methanol [36]	-	6.05	-	
Glycerol [37]	-	1.66	-	
[EMPip][BF_4][38]	-	1.13	-	
[EMPip][Br] [38]	-	1.27	-	
[EMMor][Br] [38]	-	1.29	-	
[EMMor][BF_4] [38]	-	1.13	-	
[BEPyrr][BF_4][39]	-	0.75	-	

Most of the ILs studies encompasses pure gas hydrates for CH_4 and CO_2 hydrates; however, insufficient literature available for mixed gas hydrate systems in the open literature. Ullah *et al*. [40] recently applied low concentrations (1 and 5 wt.%) of Choline-Chloride as THI for Qatari natural gas mixture and reported that 5 wt% of Choline-Chloride reduce ΔŦ up to 1.56 K. Nevertheless, 1 wt% displayed minor inhibition (ΔŦ) up to 0.5 K. Additionally, Qureshi *et al*. [41] worked with pyrrolidinium-based ILs (1-Methyl-1-Propylpyrrolidinium T`riflate [PMPy][Triflate]

and Propylpyrrolidinium Chloride [PMPy][Cl]) for Quantary mixture of Qatar natural gas for dual functional hydrate inhibitors. Their outcomes revealed that both ILs displayed dual functional impact, at 5wt%, PMPy-Cl the phase boundary shift up to 1 K. Similarly, it can also slightly improve the induction time compare to pure water [41]. Overall, an insufficient number of publications available for ILs with the mixed gas system and none of the preceding studies were emphasized the impact of AILs on CH_4 riched mixed gas hydrates.

Previously COSMO-RS software was used to determine the intermolecular interactions of ILs-water system in hydrate system [42,43]. Preceding studies suggested that in COSMO-RS, the sigma profile and hydrogen bonding are the two standout properties that justified the THI inhibition performance of ILs and other electrolytes [29,31,42,44]. Bavoh and co-workers [42] initially established that the sigma profile can determine the miscibility behaviour and hydrogen bonding ability of the ILs with water molecule which are the most fundamental properties pre-requisites for THI behaviour.

Various modelling approaches in the presence of ILs had reported earlier in the literature [19,39,45–49]. The THI behaviour induced due activity of chemical in the aqueous phase. Therefore activity coefficient approach is mainly applied. Most of the prior modelling studies only dealt with the pure gases systems like CH_4 and CO_2. Likewise, the modelling studies of mixed gas systems in the presence of ILs are scarily intermittent. Recently, our group applied the electrolyte based Dickens and Quinby-Hunt [50] model for CO_2 riched system [51]. Henceforth additional experimental and modelling investigations of ILs especially AILs on differently mixed gas hydrate systems are essential to discover the impact of AILs on phase behaviour.

Therefore, this work covers the THI performance of four AILs on CH_4 rich binary mixed gas hydrates system (70-30 mole% CH_4 + CO_2). The selection of AILs encompasses the elongation of the alkyl chain length on the inhibition performance. The thermodynamic inhibition impact of AILs + CH_4+ CO_2 for 70-30 mole % systems are measured at a temperature and pressure ranges of 276-286 K and 3.0-7.50 MPa respectively. COSMO-RS software is used to analyze AILs- water system interactions via Sigma profile graph for better understanding the inhibition mechanisms. Besides, the Clausius–Clapeyron equation also applied for calculating the hydrate dissociation

149 enthalpy of each considered system. Additionally, the electrolyte model proposed by
150 Dickens and Quinby-Hunt [50] used for predicting Hydrate Liquid-Vapor Equilibrium
151 (HL_wVE) data of a considered system in the presence of aqueous AILs solutions.

152 **METHODOLOGY**

153 ***Materials***

154 The details of chemicals use in this study are layout in Table 2. All the studies
155 chemicals are purchased from Merck milli-pore Germany and applied without any
156 further purification. The mixed gas purchased from Gas Walker Sdn. Bhd., Malaysia.
157 Deionized water was used to prepare desired concentrations of AILs in all samples.
158 For accurate weight measurements of the samples, HR-250AZ analytical balance was
159 used with an accuracy of ± 0.3 mg.

160 **Table 2**: Details of chemicals employed in this work

S.No	Name of Chemical	Formula	Purity
1	water	H_2O	Deionized
2	Mixed Gas 70.001-29.999 mole% (CH_4 + CO_2)	G	70-30 mol % (Mixed gas)
3	Tetramethyl ammonium Hydroxide	TMAOH	25.0 wt% TMAOH, 75.0 wt% H_2O (Aqueous solution)
4	Tetraethyl ammonium Hydroxide	TEAOH	40.0 wt% TEAOH, 60.0 wt% H_2O (Aqueous solution)
5	Tetrapropyl ammonium Hydroxide	TPrAOH	40.0 wt% TEAOH, 60.0 wt% H_2O (Aqueous solution)
6	Tetrabutyl ammonium Hydroxide	TBAOH	40.0 wt% TEAOH, 60.0 wt% H_2O (Aqueous solution)

161 ***Experimental details and procedure***

162 The high-pressure equilibrium cell with a volumetric capacity of 650 cm^3 used in
163 this study. The apparatus can operate within the ranges of 253–323 K and up to 20
164 MPa. The reactor is equipped with the pressure transducer (GP-M250) and temperature
165 sensor (Pt-100) to measure and record the pressure and temperature, respectively.
166 These sensor devices efficiently work with an uncertainty of ±0.01 MPa and ±0.1 K,
167 individually. Moreover, for providing adequate agitation, the mixture in the reactor is
168 stirred by the magnetic stirrer at 400 rpm. An isochoric pressure search

Thermodynamic Cycle (T-cycle) technique is adopted to detect the HL_wVE data as applied in earlier studies [32,52] especially with mixed gas hydrate systems [53,54]. Further details about the apparatus and detailed experimental procedure can found elsewhere [4,24,29,53].

HL_wVE data analysis

In this study average suppression temperature (ΔŦ) is calculated for the determination of inhibition influence of AILs on binary gas hydrate. ΔŦ has calculated via similar equation used in earlier work [11,52,55].

$$\Delta Ŧ = \frac{\sum \Delta T}{n} = \frac{\sum_{i=1}^{n} (T_{0,pi} - T_{1,pi})}{n} \quad (1)$$

where, T_0, pi denotes the equilibrium temperature of the mixed gas in a pure water sample (absence of AILs), while T_1, p_i is the equilibrium temperature of the mixed gas in the presence of aqueous AILs solutions. The values of both dissociation temperatures attained at the same p_i and n denotes to the number of pressure point considered in the experiments.

Dissociation Enthalpy (ΔH_{diss}) for mixed gas hydrate

Determination of hydrate dissociation enthalpy (ΔH_{diss}) is critical for understanding the hydrate structure and guest cage occupancy, which directly associated with the size of the guest molecule and size of the cavity. The ΔH_{diss} in this work is estimated by the Clausius-Clapeyron equation as proposed by various researchers [4,13,56–59].

$$\frac{d \ln P}{d \frac{1}{T}} = \frac{\Delta H_{diss}}{zR} \quad (2)$$

Where ΔH_{diss}, T, P, R, z, are hydrate dissociation enthalpy, temperature, pressure, universal gas constant and compressibility factor respectively. The value of *z* is calculated by using the Peng-Robinson equation of state [19,60,61] for studied mixed gas system.

COSMO-RS analysis of AILs-water system

Molecular interaction through sigma profiles of AILs and water molecules are generated in COSMO-RS software to understand the detail THI inhibition mechanism. The COSMO-RS predictions are performed using COSMOthermX, Version C2.1 software. The sigma profiles generated by selecting water and AILs

196 molecules in the compound list with the parameter file BP_TZVP_C21_0111.ctd
197 (COSMOlogic GmbH & Co KG, Leverkusen, Germany) via the lowest energy
198 conformer [42,62–66].

$$ps(\sigma) = \frac{\sum_i xip^{xi(\sigma)}}{\sum_i xi} \quad (3)$$

199 The distribution of the division given on the sigma (σ) is called σ-profile (ps(σ)).
200 The σ-profile of the solvent ps(σ), defined as the mole fraction (xi) weighted sum of
201 the σ -profiles of its compounds xi, p^{xi} respectively in Equation 3.

202 *Thermodynamic model theory*

203 To predict the hydrate phase behaviour (HL_wVE) of the studied systems, the effect
204 of additives (AILs) needs to be estimated for accurate determination of activity
205 coefficient. Since AILs are salts in the liquid phase, therefore, the electrolyte based
206 model proposed by Dickens and Quinby-Hunt [50] is employed in this work. The
207 selected model is the amended version of the Pieroen [67] model and prior applied for
208 several electrolytes studies like Amino acids [31,52] besides other ILs by Partoon *et*
209 *al*. [48] and Javanmardi *et al.* [68,69].

210 The model principally established from the traditional thermodynamic conception
211 which assumes that the amount of gas in the aqueous phase is trivial, and vice versa.
212 In the same way, the impact of AILs on the mixed gas hydrate phase boundary is
213 solitary to decrease the activity of water (a_w), and at minor temperature ranges, the
214 hydrate enthalpy of dissociation (ΔH_{diss}) is constant. The brief derivation details have
215 provided by Dickens and Quinby-Hunt [50] and Pieroen [67]. Based on this model,
216 the outcome of AILs on the gas hydrate dissociation temperature can denote as;

$$In\ a_w = \frac{\Delta H_{diss}}{nR}\left[\frac{1}{T_w} - \frac{1}{T_{AILs}}\right] \quad (4)$$

$$In\ a_w = \frac{\Delta H_{FUS(i)}}{R}\left[\frac{1}{T_{f(i)}} - \frac{1}{T_f}\right] \quad (5)$$

217 Where a_w denoted water activity, n reflected the gas hydrate hydration number
218 which taken as 5.75 due to methane-dominated gas system [19,52]. ΔH_{diss} represents
219 the hydrate dissociation enthalpies of mixed gas hydrate (60.846 kJ/mol) obtained via
220 CSMGem software, R is the universal gas constant, and T_w and T_{AILs} are the hydrate

formation temperatures in pure water and AILs solutions. $\Delta H_{FUS(i)}$ denoted as the heat of fusion of ice (6.008 KJ/mol), $T_{f(i)}$ and T_f are the freezing point temperatures of water (273.15 K) and water + AILs solutions. Freezing points of AILs (T_f) have calculated as proposed by Dickens and Quinby-Hunt [50] by using a cryoscopic constant of water as 1.853 K·kg/mol. Hereafter, merging the Eq. (4) moreover, (5), describes the temperature offset of methane hydrate phase condition and the temperature of the ice-water equilibrium condition in AILs solutions at constant pressure as follows;

$$\left[1/T_w - 1/T_{AILs} \right] = \frac{n\Delta H_{FUS(i)}}{\Delta H_{diss}} \left[1/T_{f(i)} - 1/T_f \right] \quad (6)$$

Therefore, Eq. (6) is applied to predict the hydrate dissociation temperature T_{AILs}, in the presence of aqueous AILs solutions. For the reliability of the model predictions; average absolute deviation (AAE) is also calculated by using Eq. (7).

$$AAE = \frac{1}{n} \sum_{i=1}^{n} \left| T_{Exp.} - T_{Cal.} \right|_i \quad (7)$$

RESULTS AND DISCUSSION

Influence of AILs on HL_wVE conditions of CH_4 riched mixed hydrate

The HL_wVE for of G + H_2O and G + H_2O + AILs in the presence of 10wt% aqueous AILs are reported in Table 3. To assess the impact of alkyl chain elongation on the THI; studied AILs are evaluated at moderate pressure ranges (3.0-7.50 MPa), and hydrate equilibrium curves of G + H_2O + AILs are attained in the presence and absence of various aqueous AILs solutions at 10 wt% concentrations.

Table 3: The HL_wVE points of CH_4 rich mixed gas in the absence and the presence 10 wt% AILs

AILs	Temperature (K)	Pressure (MPa)
Pure water	278.0	3.10
	281.5	4.54
	284.0	6.06
	286.1	7.55
TMAOH	276.8	3.04

	280.2	4.57
	283.0	6.10
	284.8	7.55
TEAOH	277.6	3.03
	280.6	4.53
	283.4	6.05
	285.4	7.53
TPrAOH	277.5	3.1
	281.1	4.56
	283.6	6.05
	285.5	7.55
TBAOH	278.9	3.15
	282.4	4.55
	284.9	6.05
	286.9	7.59

Expanded uncertainties U(T) = ±0.1 K; U(P)= ± 0.01 MPa (0.95 level of confidence).

The HL_wVE data of the studied binary system is depicted in Figure 1. The HL_wVE phase boundary of studied hydrate system is further compared with the commercial hydrate prediction software CSMGem and PVTsim respectively. The studied mixed gas data (see Figure 1) was found in fair agreement with the HL_wVE prediction software (CSMGem and PVTsim) data.

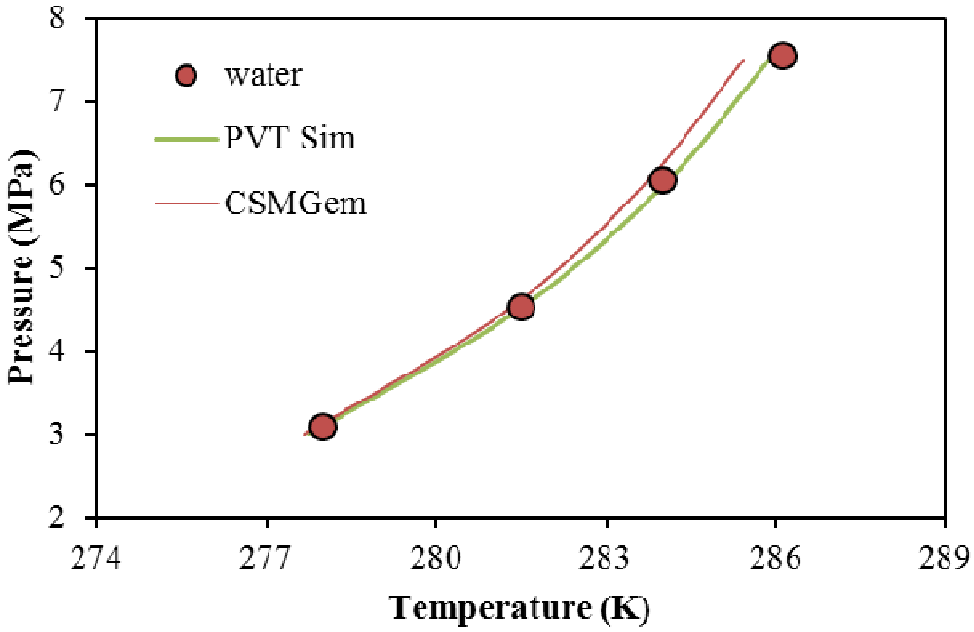

Figure 1: HL_wVE data points of CH_4 riched mixed gas (G= 70-30 CH_4 + CO_2) G+H_2O hydrates in comparisons with commercial hydrate prediction soft wares (CSMGem and PVTsim).

To evaluate the impact of alkyl chain elongation on THI performance; Figure 2 illustrates the HL_wVE data of AILs + G + H_2O hydrates at 10 wt% concentration. The results revealed that with an increase (elongation) in alkyl chain length of studied AILs, the inhibition impact appears to be significantly reduced for the studied systems. The TMAOH performed best among the considered AILs and induced maximum inhibition via shifting the HL_wVE curves towards lower temperature and higher pressure regions (see Figure 2). TEAOH and TPrAOH are also able to shift the hydrate phase equilibrium towards higher pressure and lower temperature regions for studied concentration. On the contrary, at 10 wt% TBAOH did not act as a THI in its place shifts the HL_wVE curve towards lower pressure and higher temperature regions which considerably enhance the hydrate metastable region and ultimately functioned as gas hydrate promoter. The promotion behaviour of TBAOH has observed due to the possible formation of semi-clathrate structure owing to the TBA^+ cation which has a tendency to be trapped in the hydrate cages as a non-gaseous guest at milder conditions which further discussed in later section [70,71].

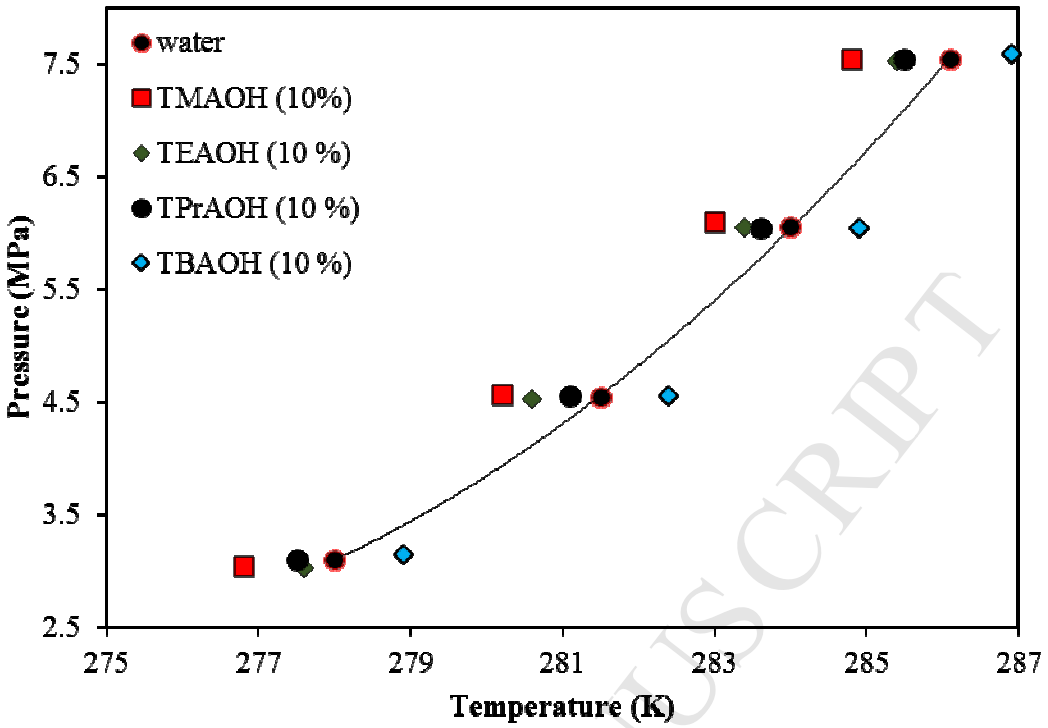

Figure 2: The HL_wVE phase behaviour of CH_4 rich mixed gas hydrates at 10 wt% AILs solutions.

To compare the quantitive impact of AILs on THI performance; the average depression temperature (ΔŦ) also reported for 10 wt% AILs solutions in Figure 3. The THI influence of AILs found in the following increasing magnitude: TBAOH < TPrAOH < TEAOH < TMAOH. Owing to the presence of the shortest alkyl chain TMAOH can deliver maximum inhibition (ΔŦ=1.28 K) among the considered AILs. On the contrary, TBAOH (ΔŦ=-0.84 K) reveal promotional result attributable to its potential semi-clathrate behaviour due to relatively elongated alkyl chain as stated in the previous studies [26,70,71].

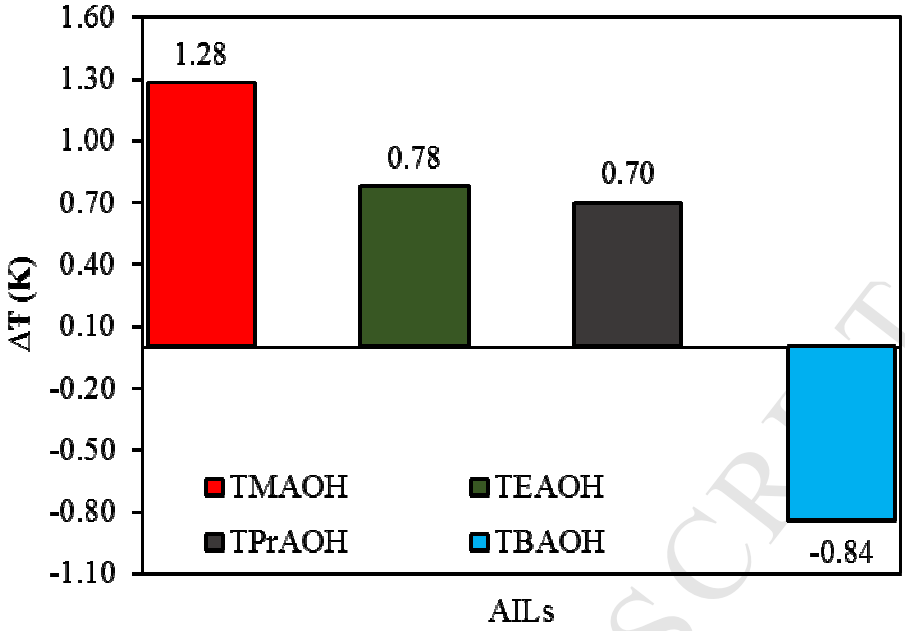

Figure 3: Average suppression temperature (ΔT) of CH4 mixed gas hydrates for 10 wt% aqueous AILs solutions.

The potential reasons for higher inhibition impact are concealed in the structure of TMAOH. TMAOH retains TMA^+ cation (shortest among the studied AILs) which merely comprises one alkyl group (methyl) in their structure together with hydroxyl (OH^-) anion which offers adequate linkage on the surface of and water gas interface. OH^- anion is already established as among the best anions that induce more hydrogen bonding with water [4,14,42] owing to their smaller nuclei size (value of 0.169 nm) which is relatively lower than all other halide anion except fluoride (F^- = 0.133 nm)[72,73]. Due to these reasons, TMAOH offer more hydrophilic behaviour compared to other studied AILs (TBAOH, TPrAOH and TEAOH) resulted in more THI inhibition [4,14,24].

To evaluate the impact of experimental pressure on the inhibition performance of AILs Table 4 presents the hydrate suppression temperature of 10 wt% aqueous AILs solutions at different experimental pressures. Results from Table 4 showed that at a studied concentration (10 wt%) of aqueous AILs solutions the inhibition performance is dependent on pressure variations (i.e., ΔT changes with experimental pressure conditions for all AILs). This is evident due to the presence of the higher amount of CH_4 in the studied mixed gas system [29]. Tariq et al. [30] also reported the similar behaviour, as their studied AILs provide higher inhibition performance at moderate pressure conditions (>6 MPa) beyond that pressure the inhibition performance significantly reduced and some of them even worked as gas hydrate promoters.

Additionally, in our earlier work [29], we observed that the inhibition performance of TMAOH also observed similar behaviour (ΔT varies with experimental pressures) for pure CH_4 hydrates, however in case of pure CO_2 hydrates there was no variation observed. Therefore, ΔT values are independent of experimental pressures.

Table 4: Suppression Temperature (ΔT) of mixed gas hydrate at different experimental pressures in the presence of 10 wt% aqueous AILs solutions

Pressure	**TMAOH (10%)**	**TEAOH (10 %)**	**TPrAOH (10 %)**	**TBAOH (10 %)**
P (MPa)	**T (K)**	**T (K)**	**T (K)**	**T (K)**
3.0	0.46	0.05	0.05	-0.81
4.50	1.51	1.05	1.02	-0.77
6.0	1.40	0.90	0.82	-1.03
7.50	0.92	0.37	0.25	-0.73
ΔT (K)	**1.28**	**0.78**	**0.70**	**-0.84**

Expanded uncertainties U(T) = ±0.1 K (0.95 level of confidence).

The acquired THI data of studied AILs are also compared with different commercial inhibitors, i.e., Methanol, Mono Ethylene Glycol (MEG) and Ethanol in Figure 4. The HL_wVE data of commercial inhibitors are generated via CSMGem. The obtained results exposed that commercial inhibitors accomplished superior THI impact compared to the considered AILs (see Figure 4), therefore suggesting that the more research on new combinations of ILs especially AILs are indispensable.

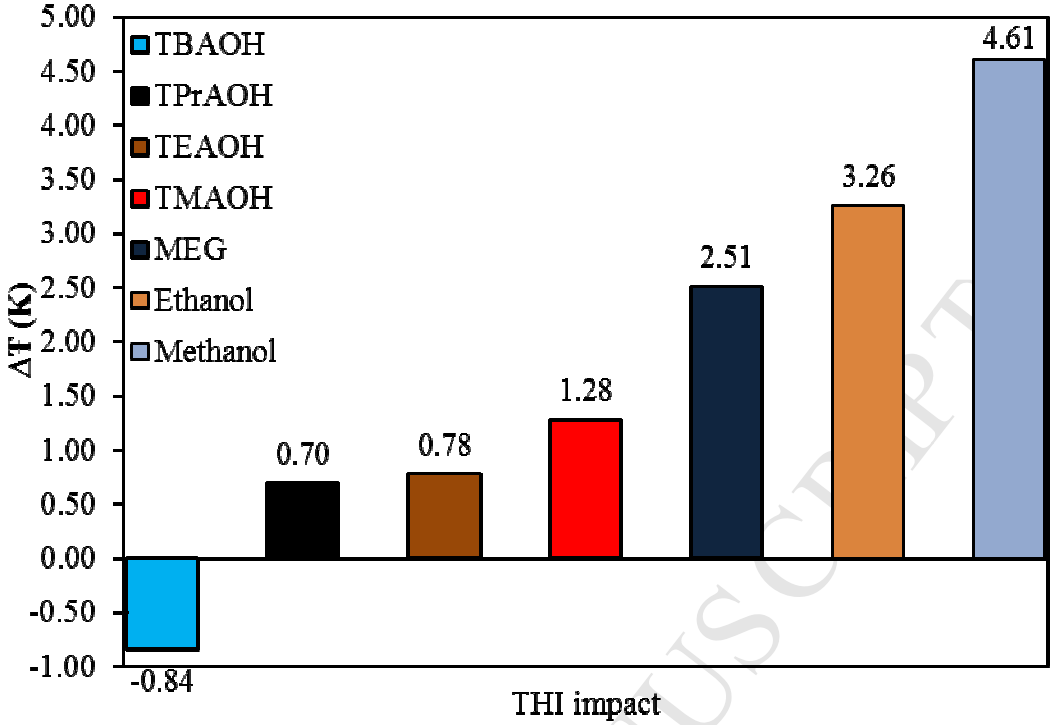

Figure 4: Comparison of THI impact (ΔŦ) of 10 wt% studied AILs with (CSMGem software predicted) commercial inhibitors data.

As it observed from the Figure 3, TMAOH displays the better inhibition among the considered AILs for CH_4 riched mixed gas hydrate systems. Therefore, the influence of different TMAOH concentrations (1, 5 and 10 wt%) further investigated, and tabulated in Table 5 and depicted in Figure 5.

Table 5: HL_wVE data of mixed gas hydrate in the presence of 1, 5 and 10 wt% concentrations of aqueous TMAOH solutions

System	TMAOH Concentration							
	0 wt%		10 wt%		5 wt%		1 wt%	
	T (K)	P (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)	*T* (K)	*P* (MPa)
G + H_2O +TMAOH	278.0	3.10	276.8	3.04	277.2	3.05	277.5	3.05
	281.5	4.54	280.2	4.57	280.6	4.51	281.0	4.51
	284.0	6.06	283.0	6.10	283.4	6.10	283.7	6.05
	286.1	7.55	284.8	7.55	285.2	7.51	285.6	7.55

Expanded uncertainties U(T) = ±0.1 K, U(P) = ±0.01 MPa (0.95 level of confidence).

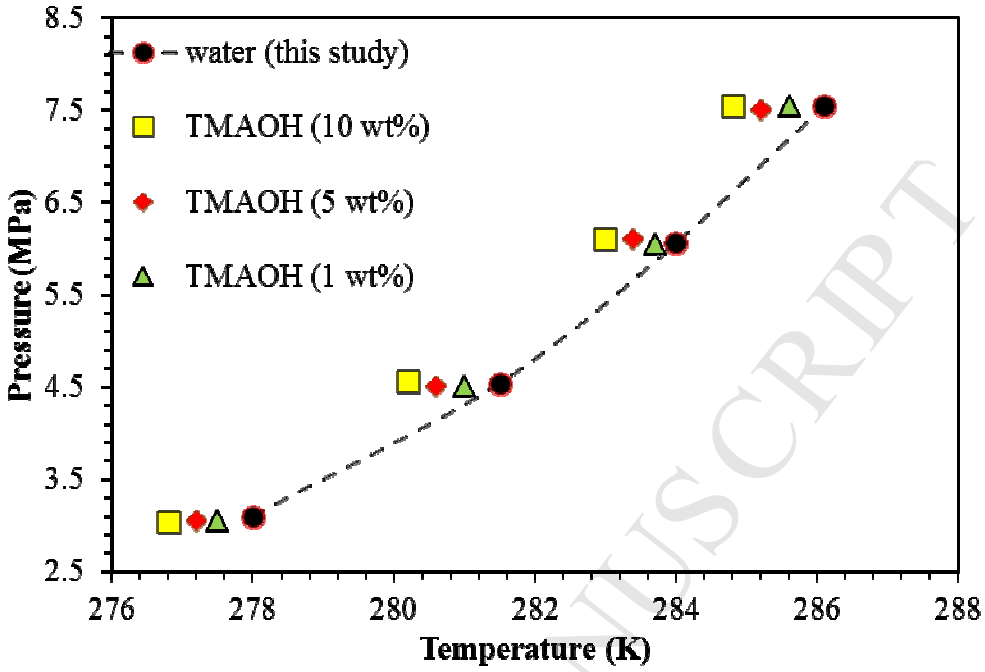

Figure 5: HL_wVE phase boundaries of CH_4 rich mixed gas in the presence of the various aqueous TMAOH concentrations.

Moreover, Table 6 reflects the suppression temperature (ΔT) of different concentration of the TMAOH at various experimental pressures for mixed gas hydrates. Results reveal that the inhibition impact of TMAOH is pressure and concentration dependent. The ΔŦ value of 10 wt% (1.28 K) concentration stretch more inhibition compares to lower concentrations of 5 (0.72 K) and 1 wt% (0.39 K). It is also noticeable that the inhibition impact also varies with the experimental pressures for each studied system (1, 5 and 10 wt %) of TMAOH. The higher inhibition (ΔT) found at moderate pressure ranges (4.50 and 6.0 MPa) perhaps due to the presence of CH_4 in the mixed gas. Subsequently, previous AIL-CH_4 studies also stated the similar behaviour for methane hydrates [29,30] as mentioned above. For further investigations, COSMO-RS study is also incorporated in next section to further investigate the alkyl chain elongation of AILs by molecular interaction with water.

Table 6: Suppression Temperature (ΔT) of CH_4 rich mixed gas hydrate in the presence of different concentrations (1, 5 and 10 wt %) of TMAOH solutions.

	TMAOH concentrations

Pressure (MPa)	10 wt%	5 wt%	1 wt%
3.0	0.46	0.29	0.05
4.50	1.51	1.22	0.87
6.0	1.40	0.98	0.63
7.50	0.92	0.37	0.02
ΔT (K)	**1.28**	**0.72**	**0.39**

Expanded uncertainties U(T) = ±0.1 K, (0.95 level of confidence).

Enthalpy of hydrate dissociation (ΔH_{diss}) for CH_4 mixed gas hydrates in the presence of AILs

The ΔH_{diss} values for all studied systems are presented in Table 7 and Table 8. It is already well recognized that both pure CH_4 and CO_2 form structure I hydrate [8,74,75]. Therefore, their CH_4 riched binary mixtures are likewise only formed structure 1 hydrates as reported in prior studies [1,19] as well. The participation of AILs in the hydrated crystalline structure identified via changes observed in the obtained ΔH_{diss}. As earlier discussed by Sloan and Koh [1] that the enthalpy of hydrate dissociation is predominantly affected by the cage occupancy of guest molecule. Thus, as the ΔH_{diss} of studied AILs are not altered in the presence of all AILs except TBAOH, it could be established that AILs are not contributing to the hydrate crystalline structure. However, in case of TBAOH ΔH_{diss} is noticeable changes in-comparisons with pure water which is attributed owing to the semi-clathratic nature of TBAOH as reported by the previous studies [70,71]. This enlightened the contribution of TBAOH molecules in the formation of hydrate cages to form semi-clathrate hydrates due to the presence of TBA^+ cation as comprehensively define by Shimada and co-workers prior [76]. Moreover, as the ΔH_{diss} is in the range of sI hydrate, it could be concluded that apart from TBAOH, only s1 hydrates are formed during these experiments.

Table 7: Calculated molar enthalpies ΔH_{diss} (kJ/mol) of hydrate dissociation in the presence and absence of 10wt% aqueous AILs solution for CH_4 rich mixed gas hydrates at various equilibrium pressures

Pressure	10 wt% aqueous AILs solutions				
(MPa)	Water	TMAOH	TEAOH	TPrAOH	TBAOH
3.0	64.50	65.56	65.82	65.01	75.88
4.50	61.26	61.96	61.02	61.52	72.14

6.0	58.09	58.72	56.31	58.39	67.67
7.50	55.37	55.93	52.03	55.57	63.28
Average ΔH_{diss}	**59.80**	**60.54**	**58.80**	**60.12**	**69.74**

Expanded uncertainties U(T) = ±0.1 K, U(P) = ±0.01 MPa, U(mass fraction) = ±0.0001 g, U(H) = ± 1.2 kJ·mol-1 (0.95 level of confidence).

Table 8: Calculated molar enthalpies ΔH_{diss} (kJ/mol) of TMAOH at different concentrations (1, 5 and 10wt %) for CH_4 rich mixed gas hydrates at various equilibrium pressures

Pressure (MPa)	**TMAOH composition**			
	0 wt%	**1 wt%**	**5 wt%**	**10 wt%**
3.00	64.50	65.23	65.42	65.56
4.50	61.26	61.87	62.01	61.96
6.00	58.09	58.64	58.79	58.72
7.50	55.37	55.83	56.02	55.93
Average ΔH_{diss}	**59.80**	**60.39**	**60.56**	**60.54**

Expanded uncertainties U(T) = ±0.1 K, U(P) = ±0.01 MPa, U(mass fraction) = ±0.0001 g, U(H) = ± 1.2 kJ·mol-1 (0.95 level of confidence).

COSMO-RS Analysis of AILs-Water System

Commonly, the chemicals which can form efficient hydrogen bonding with water are apparently better thermodynamic inhibitors. The main idea to apply COSMO-RS in this study to acquires the sigma profile data of the studied systems (AILs-water). The sigma profile data are generated to facilitate the better understanding of the alkyl chain elongation impact on the hydrophilicity and hydrogen bonding interaction of studied AILs as illustrated in Figure 6. Moreover, the sigma profiles of commercial THI inhibitors, i.e., methanol, MEG and ethanol are also added in Figure 6 to understand the THI behaviour. According to Klamt [43], the Sigma profile can divide into three (3) interactions regions. The first region at the left side outlines the most electropositive area (i.e. H-bond donor). Whereas nonpolar area is the lies in the middle (between -1.0 e/nm^2 and 1.0 e/nm^2) and the right side represents highly electronegative, i.e. act as H-bond acceptor region [42,62,66,77] as shown in Figure 6.

It is a observe from sigma profile results in **Error! Reference source not found.**6 that water possessed extraordinary H-bonding donor and acceptor affinity in both polar regions; this tendency ascends due to the presence of lone pairs of the oxygen besides the two hydrogen atoms in its structure. Sigma profiles of conventional

inhibitors revealed that they possess extended and similar sigma profile peaks length like water (mainly methanol) which can efficiently interact with water with dominant hydrogen-bond exchange which ensued in higher miscibility.

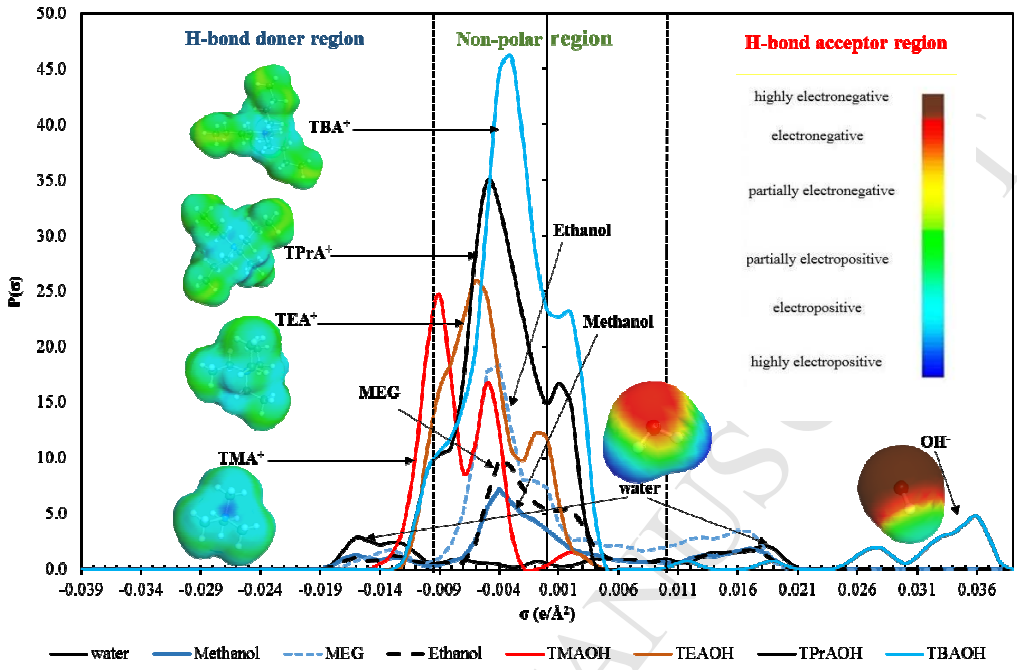

Figure 6: COSMO-RS generated sigma profiles and sigma surfaces of studied AILs, conventional inhibitors and water systems.

In case of AILs, the AILs are having difference in the peak height in the same regions provide better miscibility with each other, increase in peak difference results towards lesser miscibility among them. The AILs cation having shortest alkyl chain, i.e. TMA^+ shows the highest H-bond donor ability due to engaging some area in the H-bond donor region together with lowest peak difference (21.818) among water in nonpolar regions. On the contrary, The OH^- anion shows a peak on the extreme right side of Figure 5 which indicated its powerful H-bond acceptor ability. Another essential reason makes OH^- more suitable anion is there lowest peak difference (2.931) in H-bond acceptor region with a water molecule. The minor difference among peaks together higher H-bond acceptor affinity results in the form of potentially better hydrate inhibition performance. Moreover, the presence of TMA^+ cation rises the hydrophilicity of TMAOH consequent in higher thermodynamic inhibition impact compared to the other studied AILs. Furthermore, TMAOH possesses TMA^+ cation which contains only one alkyl group (methyl) which also offer sufficient linkage at the surface of gas and water interface, display comparatively hydrophilic behaviour compared to higher alkyl chain AILs [25,29].

411 The peak difference further extended as the alkyl chain length of the AILs increases
412 as in the case of TEAOH, TPrAOH and TBAOH [12]. Interestingly, the trend of
413 sigma profile data analysis further justified the THI inhibition behaviour of
414 considered AILs.
415 Preceding Literature [14,25] has previously recognized that the THI behaviour is
416 favourably reliant on the hydrogen bonding ability of anion like OH^- together with the
417 elongation of cations alkyl chain length as confirmed via sigma profile analysis (see
418 Figure 5. Apparent thermodynamic inhibition of AILs is very sensitive to the change
419 in cation, primarily due to microscopic level hydrogen bonding interactions of
420 between AILs and water molecules [78]. The hydrogen bonds and electrostatic
421 interactions of AILs considerably lower the activity coefficient of water, and therefore
422 lead to robust THI inhibition [79]. Thus the better hydrate inhibition performance of
423 TMAOH (as witnessed in Figure 3, and Figure 3, ΔT= 1.28 K) is due to the presence
424 of shortest alkyl chain cation (methyl $-CH_3$) [TMA^+] among all the studied system as
425 confirmed by the Figure 5. Additionally, Kurnia *et al.*[80], stated the increase in the
426 size of alkyl chain length increase the aliphatic-moieties associated with the cation
427 core of AILs leads towards the hydrophobicity of AILs and hence to decline the AILs
428 mutual miscibility with water which attributed due to the influence of cations in the
429 considered AILs. Moreover, the presence of OH^- functional group, significantly
430 increases the nonideality of the system by altering the chemical potential as revealed
431 by elsewhere [21]. Nevertheless, both conventional inhibitors and AILs show peaks in
432 all the sigma profile regions like water. However, COSMO-RS data further
433 corroborated the superior THI impact of conventional over studied AILs.

434 *Thermodynamic modelling of CH_4 riched mixed gas hydrate in the presence of AILs*

435 The considered electrolyte model (Dickens and Quinby-Hunt [50] model) is
436 utilize to predict the HL_wVE data for studied systems with AILs solutions. Since the
437 considered model use freezing point (T_f) depression temperatures of the electrolyte,
438 the T_f of the studied AILs solutions are calculated as proposed by Dickens and
439 Quinby-Hunt [50] and reported in Table 9.

$$T_f = -k_f(m)(i) \tag{8}$$

440 where, k_f represents the cryoscopic constant of water as 1.853 K·kg/mol, m denoted
441 the molality of the AILs, and i represents the ionic strength of the AILs.

Table 9: The calculated freezing point temperatures T_f (K) of studied AILs solutions.

AILs concentrations	TMAOH	TEAOH	TPrAOH	TBAOH
1 wt%	272.77 K	-	-	-
5 wt%	271.87 K	-	-	-
10 wt%	270.73 K	271.60 K	271.99 K	272.20 K

Expanded uncertainties U(T) = ±0.1 K, (0.95 level of confidence).

As is observed from Table 9 that the freezing point of the AILs systems increased with the elongation of the alkyl chain. As a result, TMAOH offers the lowermost freezing point which endorsed in the form of superior THI inhibition. The predicted and experimental HL_wVE data points for 10 wt% aqueous AILs solutions depicted in Figure 6. Furthermore, the modelling is extended to the various concentrations of TMAOH solution and presented in Figure 7.

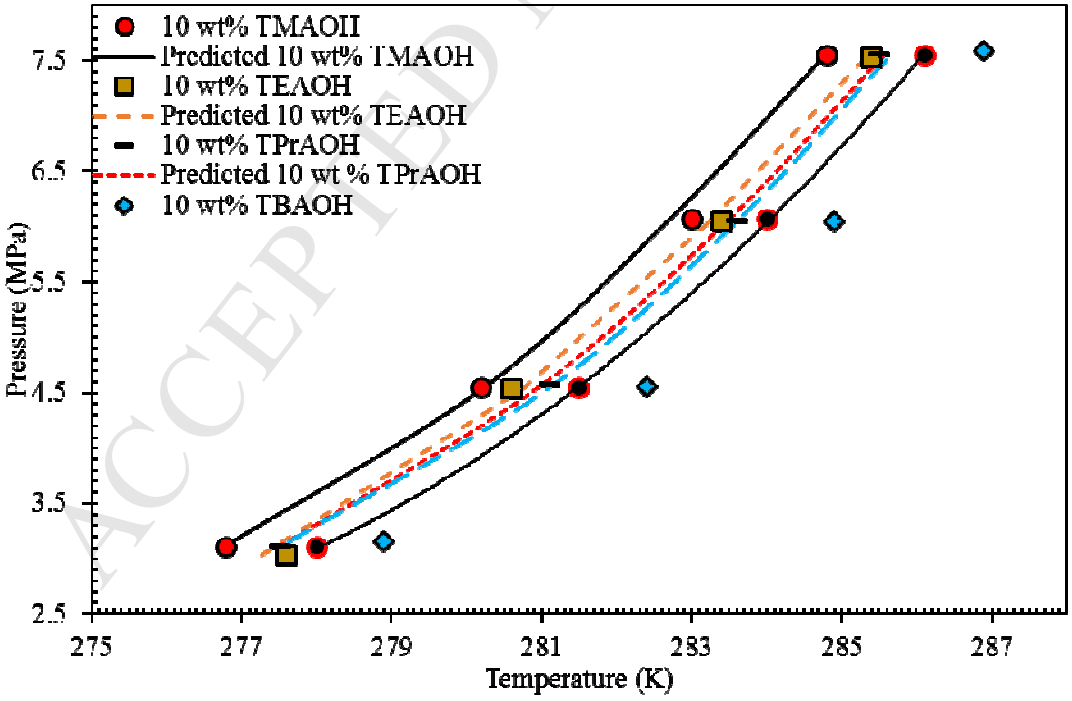

Figure 7: Experimental and predicted HL_wVE data points for 10 wt% AILs systems with CH_4 riched mixed gas.

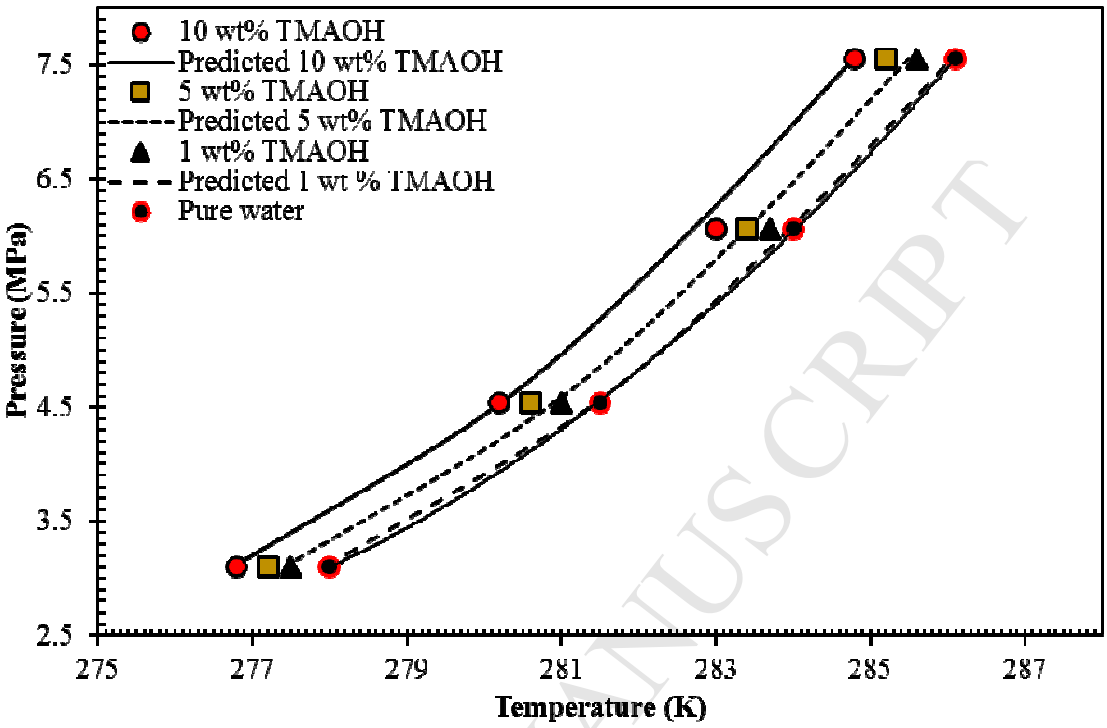

Figure 8: Experimental and predicted HL_wVE data for 1, 5 and 10 wt% TMAOH with CH_4 riched mixed gas.

As demonstrated in the above figures, the predicted HL_wVE modelling results are in satisfactory agreement with experimental data. Table 10 further presented the average absolute error for prediction of CH_4 rich mixed gas HL_wVE points of studied systems. Also, robust correlations with R^2 values < 0.99 at 95 % confidence level attained among the experimental and predicted HL_wVE data in the presence of shorter alkyl chain AILs (TMAOH, TEAOH and TPrAOH). Owing to semi-clathratic nature of TBAOH, the existing model is not capable of pertinent the TBAOH behaviour. As stated earlier, the considered electrolyte model established upon the freezing point depression temperatures of the AILs. Ideally, TBAOH supposes to provide slight inhibition at 10wt% concentration instead it delivers hydrate promotional impact attributed due to its semi-clathratic nature caused in overprediction as evident in AAE value of 1.28 K (see Table 10). The enthalpy of TBAOH data in this study also confirmed the semi-clathratic nature of TBAOH which previously reported for different gases systems [26,70,81,82]. It can also conclude from TBAOH result that

the existing model is not appropriate for semi-clathrate hydrates. Moreover, the accuracy of the model at low concentration (i.e. 1wt% TMAOH) is found least precise than other concentrations perhaps owing to a smaller extent of freezing point depression at 1 wt% aqueous TMAOH solution. Overall, this can be concluded that, in hydrate formation conditions, aqueous AILs have the same behaviour as electrolytes. Therefore, the existing model could employed efficiently or modified for the modelling of the HL_wVE conditions in the presence of different ionic liquids for other hydrate formers.

Table 10: Predicted HL_wVE points in the presence of studied AILs systems.

System	Temperature range (K)	No. data point	AAE (K)	R^2
10 wt% aqueous AILs solutions				
TMAOH	276.7-284.7	4	0.10	0.998
TEAOH	277.2-285.3	4	0.18	0.997
TPrAOH	277.5-285.5	4	0.08	0.999
TBAOH	277.6-285.7	4	1.26	0.999
TMAOH solutions				
1 wt%	278.0-286.1	4	0.40	0.999
5 wt%	277.4-285.5	4	0.20	0.998
10 wt%	276.7-284.7	4	0.10	0.998

CONCLUSION

In this study, the HL_wVE behaviour of CH_4 rich binary mixed gas in the presence of four AILs are reported via experimental and modelling approaches. Results indicated that in the presence of shorter alkyl chain AILs (TMAOH, TEAOH and TPrAOH at 10wt % concentration) the hydrate phase boundary CH_4 riched gas moves to higher pressure and lower temperature regions. Conversely, TBAOH displayed hydrate promotional influence in this study. The average suppression temperature (ΔT) between 10wt% AILs systems ranged between 1.28 K (TMAOH) to -0.84 K (TBAOH) within the studied pressure range (1.90-5.10 MPa). It is apparent from the

accomplished results that the THI inhibition profoundly linked to the alkyl chain length of cation (elongation) of AILs. Thus, shorter alkyl chain delivers enhanced thermodynamic inhibition in comparison to higher alkyl chain length AILs. The THI impact of TMAOH (best found AIL in this study) also extended to various concentrations (1, 5 and 10 wt %) and found that THI inhibition reduced with decreased concentrations of TMAOH. Sigma profile data of considered AILs from COSMO-RS provide additional justification on the influence of alkyl chain length (elongation) of AILs on THI inhibition. Moreover, the dissociation enthalpy of CH_4 riched mixed gas (CH_4 + CO_2 + AILs-water) also reported for all the studied systems. Apart from TBAOH (semi-clathrate), the enthalpy data of all other (considered) AILs are in the range of the structure I hydrate. Apparently; this also endorses that shorter alkyl chain AILs do not partake in the hydrate cage structures. Furthermore, the electrolyte based thermodynamic model applied to predict the HL_wVE data of CH_4 riched mixed gas hydrates in the presence of studied AILs; except for TBAOH, all the considered AILs exhibited a good agreement with experimental data.

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Research Highlights

- Elongation of AILs alkyl chain attributed decline in THI.
- Enthalpy of hydrate dissociations data reported for CH_4 riched mixed gas systems.
- COSMO-RS based sigma profile analysis justified the THI behavior of studied AILs.
- The experimental and model predicted HL_wVE data are found to be in good agreement.